

# **Equation of State for Inhomogeneous Solution Close to the Separation Critical Point<sup>1</sup>**

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## ABSTRACT

Experimental investigations of the kinetics of equilibrium gravity effect establishment in the binary solution of methanol-hexane were carried out by using refractometry method for temperatures lower than separation critical temperature  $T < T_c$ . Both the height equilibrium dependencies of refractive index gradient  $dn/dz(z, t_{\text{equilibr}})$  and non-equilibrium ones  $dn/dz(z, t)$  for different times  $t$  after beginning of the thermostating were found as a result of the experiment.

The analysis of the obtained results showed that the relaxation properties of the system at the different heights are determined not by the single relaxation time  $\tau(z)$  but by the set of the relaxation times  $\Sigma \tau_i(z_j, t)$ . The relaxation time  $\tau(z, t)$  at the separate heights  $z$  is also decreased while the system approaching to the equilibrium state. On the basis of the obtained data the height dependence of relaxation times is analyzed for investigated solution as the system approach to the equilibrium. The average relaxation time  $\overline{\tau(z)}$  is shown to be decreased when approaching to the phase interface ( $z=0$ ).

The dynamic equation of non-equilibrium state for substance under gravity close to the phase interface of binary solution was proposed with help of the fluctuation theory of phase transitions on the basis of assumption that every non-equilibrium height distribution  $dn/dz(z, t)$  corresponds to the equilibrium value  $dn/dz(z, \Delta T)$  for a certain temperature  $T$ , here  $\Delta T = T - T_c$  is the deviation of the temperature  $T$  from the critical temperature  $T_c$ .

**KEY WORDS:** critical point; equation of state; inhomogeneous solution; non-equilibrium state; phase transitions

## 1. INTRODUCTION

According to the fluctuation theory of phase transitions in fluid systems [1] the correlation length  $R_c$  grows indefinitely as the critical point is approached. Hence the time of equilibrium establishment  $t_e$  in system related with the relaxation time as  $t_e \sim \tau \sim R_c$  is also bound to increase. This conclusion was made for homogeneous systems, however it breaks down for spatially inhomogeneous systems exposed to the gravitational field near the critical point [2-3].

A large variety peculiarities of behavior for inhomogeneous fluids not being observed for homogeneous systems were first revealed by performed by us experimental investigations of kinetics of equilibrium establishment in such inhomogeneous systems [2-3] for temperatures over the separation critical temperature  $T > T_c$ .

Firstly, a non-monotonous temperature dependence of equilibrium establishment time  $t_e(\Delta T)$  was discovered for inhomogeneous substance under gravity [2]. The greatest time  $t_e = \max$  corresponds to a temperature  $\Delta T > 0$  rather than to the critical temperature  $\Delta T = T - T_c = 0$ . It was firstly therewith proved that time  $t_e$  depends not just on relaxation time  $\tau(\rho_c) \sim \Delta T^{-\nu}$  but on thickness of layer  $\Delta z$  of liquid with critical density  $\rho_c$  which varies with temperature as  $\Delta z \sim \Delta T^{\beta\delta}$  ( $t_e \sim \tau \cdot \Delta z \sim (\Delta T)^{\beta\delta-\nu}$ ). Secondly, the non-monotonous height dependence of relaxation time  $\tau(z)$  of inhomogeneous liquid under gravity is obtained. Maximum value of the  $\tau(z)$  corresponds not to the level  $z=0$  with critical density  $\rho_c$  of substance investigated but to a height  $z \neq 0$ , in the vicinity of which isotherms of refraction index gradient  $dn/dz$  intersect each other when system passing to the equilibrium state. It was also first founded [3] that the relaxation properties of inhomogeneous liquid at some height  $z$  are determined not by a single relaxation time

but by a set of times  $\Sigma \tau_i(z_j)$  which characterizes the whole inhomogeneous system under gravity.

The purpose of the given work is the sequel of these experimental investigations of peculiarities of kinetic of equilibrium establishment in spatially inhomogeneous fluid systems near the critical points. In particular it is connected with working out of a time-state equation of such non-equilibrium fluid under the external gravitational field.

## **2.MEASUREMENTS**

Experimental techniques and equipment have been detailed in works [2,4]. The binary methanol-hexane solution with critical mass fraction of methanol  $x=0.31$  was poured into temperature-controlled optical cell with parallel glass. The mass of the solution was such that the gas phase was over the investigated substance at all temperatures being studied.

The solution was heated initially from double-phase state at room temperature  $T=293$  K to the critical phase separation temperature  $T_c=315.7$  K and was carefully thermostated at this temperature with an accuracy 0.01 K as long as the refractive index gradient was unchanged at all heights of inhomogeneous solution. A temperature at which the phase interface of the solution components disappeared was taken as the critical one.

Thereafter the given inhomogeneous but equilibrium system was cooled rapidly from the critical temperature to some temperature  $T < T_c$  and was thermostated for a long time until it turned into another equilibrium state at temperature  $T$ . Period of time after which the value  $dn/dz(z)$  practically wasn't changed was taken as the equilibrium time  $t_e$ . The height dependence of the refractive index gradient  $dn/dz(z)$  of the solution was continuously changed with time  $t$  when system passing to the equilibrium state. It

was investigated while thermostating at the temperature  $T$  .

### 3. RESULTS.

#### 3.1. Kinetics of equilibrium establishment.

Fig. 1 gives projections of kinetics of change of symmetrized refractive index gradient values  $dn/dz(z,t) = \frac{1}{2} (dn/dz(z>0,t) + dn/dz(z<0,t))$  (values  $dn/dz$  were taken at symmetric heights about the phase interface  $z=0$ ) at different heights  $z$  of cell with inhomogeneous methanol-hexane solution in system going to the equilibrium state at the temperature  $\Delta T = T - T_c = -1.55$  K. The equilibrium state of substance with height dependence  $dn/dz(z,t)$  is described by the lowest curve. Value  $dn/dz$  is seen to fastest change at the level of phase interface  $z=0$  when passing to the equilibrium state. The derivative  $dn/dz(z)$  is changed with time  $t$  much more weakly at heights  $|z| \approx 6$  mm. Kinetics of the derivative  $dn/dz(z)$  change has qualitatively the same character at others temperatures  $\Delta T$ .

On the basis of these data the relaxation times  $\tau(z)$  of the derivative  $dn/dz(z,t)$  at different heights of investigated system were calculated by using relaxation relation:

$$\Delta dn/dz(z,t) = dn/dz(z,t) - dn/dz(z,t_e) = \Delta dn/dz(z,t=0) \cdot \exp(-t/\tau) \quad (1)$$

These calculations are shown on Fig. 3. Time-dependencies  $\ln(\Delta dn/dz)(t)$  is seen to be not linear functions of time. It can be suggested from this that kinetics of equilibrium establishment at every separately taken height of the inhomogeneous system is characterized not by a single relaxation time  $\tau(z)$  but by the set of relaxation times  $\Sigma \tau_i(z_j)$ . Whole inhomogeneous system under gravity is determined by this set of times. This is due to the fact that the relaxation properties of separately chosen layer of the

substance are certain dependent on solution density and concentration which are continuously changing with time at this height when inhomogeneous system going to the equilibrium state. It should be in addition that kinetics of equilibrium establishment at some separate height  $z_i$  also depends on relaxation properties of all others substance layers through which the substance is transported when system going to equilibrium state.

It also follows from Fig. 3 that the average time  $\overline{\tau(z)} = [\ln(dn/dz(z, t_1)) - \ln(dn/dz(z, t_2))] / [t_2 - t_1]$  at every height  $z$  monotonically decreases when the phase interface level  $z \rightarrow 0$  is approached.

As is obvious from Fig. 3 the curvature of curves  $\ln \Delta dn/dz(z, t)$  increases with time. This testifies to the fact that relaxation time  $\tau(t)$  of the refractive index gradient  $dn/dz$  (it's defined by the slope of the tangent to the curve  $\ln \Delta dn/dz(z, t)$ ) decreases when approaching to the equilibrium state. That is, the process of equilibrium establishment in system is accelerated as the equilibrium state is approached. Such behavior of  $\tau(z, t)$  is explained by departure of concentration and density at each height  $z$  of the solution from the critical values at temperatures  $T < T_c$  when approaching to the equilibrium state. This is the main reason of relaxation time decreasing.

### **3.2 Non-equilibrium scaling function.**

Presented above data on kinetics establishment of equilibrium values of concentration gradient  $dc/dz(z, t) \sim dn/dz(z, t)$  were used for construction of dynamic equation of state for substance under gravity near the critical point. It was suggested for analysis of data  $dc/dz(z, t)$  that the non-equilibrium characteristics of solution at different times  $t$  correspond to the analogous equilibrium properties of substance for some

definite temperatures  $\theta=(T-T_c)/T_c$ .

That is the temperature dependence  $dc/dz(z,t) \sim \theta^{-\gamma}$  may be proposed instead of time-dependence  $dc/dz(z,t)$  near the phase interface. Moreover, the value of temperature  $\theta_i$  can be calculated by using relation:

$$\frac{dc}{dz}(z, t_i) \cdot \left[ \frac{dc}{dz}(z, t_{\text{equilibr}}) \right]^{-1} = \left( \frac{\theta_i}{\theta_{\text{equilibr}}} \right)^{-\gamma}. \quad (2)$$

The analysis of obtained data shows that the time  $t_i$  depends on temperature  $\theta_i$  as  $t_i \sim \theta^{1/\beta\delta}$  as a first approximation (here  $\beta \approx 1/3$ ;  $\delta \approx 5$  are critical indexes of fluctuation theory [1]). Taking this into account on the basis of obtained data  $dc/dz(z,t) \sim dc/dz(z,\theta)$  the scaling equation of non-equilibrium fluid was proposed as follows:

$$\frac{dc}{dz} = \theta^{-\gamma} \Phi_1 \left( \frac{z}{\theta^{\beta\delta}} \right) = t^{-\gamma/\beta\delta} \Phi_2 \left( \frac{z}{t} \right). \quad (3)$$

Here  $\Phi_1$  and  $\Phi_2$  are the scaling functions of the scaling arguments  $z_1^* = z/\theta^{\beta\delta}$  and  $z_2^* = z/t$ ;  $\gamma \approx 5/4$  is the critical index of fluctuation theory [1]. Form of this scaling function is shown on Fig. 4. The data  $dc/dz(z,t)$  (Fig. 2) at height range  $z=0 \div 2$  mm, at which the solution concentration  $\Delta c = (c - c_c)/c_c$  is within  $\Delta c = (0 \div 0,3) \ll 1$  were used for it building up. Three-dimensional surface  $dc/dz(z,t)$  (Fig. 2) is seen to be turned out to the single line  $\Phi_1(z_1^*)$  of scaling argument  $z_1^*$  for these values of the concentration of the methanol-hexane solution:

$$\Phi_1^{-1}(z_1^*) = 7.018 + 85.41 \cdot \left| \frac{z}{t} \right|^\gamma \quad (4)$$

The range of action of this scaling equation is marked out by curve, which limit concentration  $\Delta c \leq 0.3$ . Ginsburg criteria is not executed at the range of concentrations  $\Delta c > (0.4 \div 0.8) \approx 1$  when order parameter  $\Delta c$  can't be defined as the small one. In this case

the inhomogeneous system goes out of fluctuation range and can't be described by the scaling equation (3).

From the performed experimental investigations it may be deduced that kinetics of equilibrium establishment at every separately chosen height of inhomogeneous system is characterized not by a single relaxation time  $\tau(z)$  but by the set of times  $\Sigma\tau_i(z_j)$ . This is due to the fact that the relaxation properties of separately chosen layer of the substance are certain dependent on solution density and concentration which are continuously changing with time at this height when inhomogeneous system going to the equilibrium state. The average time  $\overline{\tau(z)}$  at every height  $z$  monotonically decreases when the phase interface level  $z \rightarrow 0$  is approached. Relaxation time  $\tau(t)$  of the refractive index gradient  $dn/dz$  decreases at temperatures  $T < T_c$  as the equilibrium state is approached. That is, the process of equilibrium establishment in system is accelerated when going to the equilibrium state.

The inhomogeneous non-equilibrium system of the binary methanol-hexane solution under gravity within of concentrations  $\Delta c = 0 \div 0.3$  is shown in the paper to be described by the dynamic scaling equation of state  $\frac{dc}{dz} = t^{-\gamma/\beta\delta} \Phi_2\left(\frac{z}{t}\right)$ .



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## FIGURE CAPTIONS

Fig. 1. Projection of kinetics of change of the symmetrized refractive index gradient  $dn/dz$  height dependence of inhomogeneous methanol-hexane solution at the temperature  $\Delta T = -1.55$  K below the critical phase separation temperature for different times  $t$  after beginning of thermostating.

Fig. 2. Kinetics of change of the symmetrized refractive index gradient  $dn/dz$  height dependence of inhomogeneous methanol-hexane solution at the temperature  $\Delta T = -1.55$  K below the critical phase separation temperature.

Fig. 3. Derivative  $dn/dz$  change with time of inhomogeneous methanol-hexane solution at different heights  $z$  about the level with critical density at temperature  $\Delta T = -1.55$  K below the critical temperature.

Fig. 4. Scaling function of non-equilibrium methanol-hexane solution under gravity near the phase interface in the concentration range of methanol-hexane  $\Delta c = (0 \div 0.3) \ll 1$ .







